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[Title of Invention]

A CO-selective oxidizing catalyst in hydrogen gas, its manufacturing method, and a method to remove CO from the hydrogen gas.

[Summary]

[Objective]

To offer a CO-selective oxidizing catalyst in hydrogen gas that contains hydrogen gas as its major component but also includes CO and water: the said CO-selective oxidizing catalyst prevents aggregation of water that is contained in the hydrogen gas and can adequately reduce the CO concentration in the hydrogen gas by selectively oxidizing the aforementioned CO.

[Method to achieve the objective]

A CO-selective oxidizing catalyst in hydrogen gas, in which a complex oxide of base metals such as copper containing platinum group metals (e.g., palladium and ruthenium) and rare earth metals (e.g., cerium and neodymium) is dispersed on the surface of a composite ceramic carrier through activated alumina.

[Scope of the patent claims]

[Claim 1]

A CO-selective oxidizing catalyst in hydrogen gas in which a complex oxide of base metals containing platinum group metals and rare earth metals is dispersed on the surface of a composite ceramic carrier through activated alumina.

[Claim 2]

A CO-selective oxidizing catalyst in hydrogen gas that is defined by Claim 1 in which the platinum metals are palladium and ruthenium.

[Claim 3]

A CO-selective oxidizing catalyst in hydrogen gas that is defined by Claim 2 in which palladium is in a form selected from palladium chloride, palladium nitrate, and dinitrodiamine palladium and ruthenium is in a form selected from ruthenium chloride and ruthenium nitrate.

[Claim 4]

A CO-selective oxidizing catalyst in the hydrogen gas defined by Claim 1 in which the base metal is copper.

[Claim 5]

A CO-selective oxidizing catalyst in the hydrogen gas defined by Claim 1 in which the rare earth metal is cerium and/or neodymium.

[Claim 6]

A CO-selective oxidizing catalyst in the hydrogen gas defined by Claim 5 in which cerium and/or neodymium is in the form of cerium oxide and/or neodymium oxide and the ratio of the

maximum X-ray peak of other metal oxides to those of cerium oxide and /or neodymium oxide is less than 0.01.

[Claim 7]

A method to produce a CO-selective oxidizing catalyst in the hydrogen gas: in manufacturing the CO-selective oxidizing catalyst in hydrogen gas that is defined by any one of Claims 1 through 6, the complex oxide of base metals containing a platinum group metal and rare earth metals is one that is produced through monoxycarbonates that are generated from a hydration reaction of a carbonate.

[Claim 8]

A method to produce a CO-selective oxidizing catalyst in hydrogen gas that is characterized by the following: a platinum group metal salt, copper salt, and rare earth metal salt are allowed to form coprecipitates through a hydration reaction, using heated vapor; then sintered in air to obtain a complex oxide of base metal containing platinum group metals and rare earth metals. The oxide is then kneaded with activated alumina to form a slurry, which is used to coat a composite ceramic carrier, then sintered in an oxidizing gas at 350 to 500°C.

[Claim 9]

A method to remove CO contained in hydrogen gas that is characterized by the following: A gas containing hydrogen as its major component but also containing CO is mixed with oxygen to form a gas mixture. This mixture of gases is brought into contact with the CO-selective oxidizing catalyst defined by any one of Claims 1 through 6 to oxidize CO selectively by converting CO to CO₂, thus removing the CO in the gas that is composed mainly of hydrogen but also contains CO.

[Claim 10]

A method to remove CO contained in hydrogen gas, defined in Claim 9, in which a CO-selective oxidizing reaction is allowed to take place in a temperature range of 100 to 200°C.

[Detailed description of the present invention]

[0001]

[The technological field to which the present invention belongs]

The present invention concerns a CO-selective oxidizing catalyst contained in hydrogen gas—a catalyst that is suitable for selective oxidation of CO in a gas that is composed mainly of hydrogen but also contains CO, a method to manufacture such a catalyst, and a method to remove CO from hydrogen gas. To define further, it is a CO-selective oxidizing catalyst in a hydrogen gas—a catalyst suitable for reducing the CO content in a hydrogen gas by selectively

oxidizing and removing the CO from the hydrogen gas that is obtained by refining materials such as methanol supplied to a fuel electrode of a fuel cell in a fuel cell generator, a method to manufacture such a catalyst, and a method to remove CO in a hydrogen gas.

[0002]

Fuel cell generators have been designed with a fuel electrode and an oxidizing electrode installed, one at each side of the electrolyte; and hydrogen and oxygen are supplied to the said fuel electrode and oxidizing electrode, respectively. Such generators have attracted attention as automobile batteries because they are less likely to pollute the atmosphere, lose minimum amounts of energy, and are easy to operate.

[0003]

Diverse types of fuel cells are available for different forms of fuels, electrolytes, and operating temperatures. Among them, the so-called hydrogen-oxygen fuel cell that uses hydrogen as a fuel and oxygen as an oxidizing agent is thought to be highly promising. Fuel cells operating at low temperatures and that use solid polymers for electrolytes are being developed and some have been put to practical use. Wider application of these fuel cells is expected in the near future.

[0004]

For such fuel cells, especially those operating at low temperatures, platinum (a platinum catalyst) is used as an electrode.

[0005]

However, platinum that is used as an electrode is readily poisoned by CO: if the CO content of the fuel exceeds a certain level, the generating capacity is reduced or completely lost. This serious problem, the deterioration of the electrode caused by CO, is more evident at lower temperatures; therefore it becomes a truly serious problem for those fuel cells that are operated at low temperatures.

[0006]

It is desirable that the fuel for a fuel cell that uses a platinum electrode catalyst be pure hydrogen. However, it is a common practice to use hydrogen containing gases that are obtained by steam-refined alcohol-type fuels (such as methanol), which are inexpensive, convenient to store, and readily available through a public supply system. It is expected that such fuel cell generating systems incorporating a refining device will be utilized more extensively in the near future.

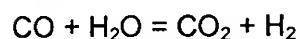
[0007]

However, such a refined gas, in addition to hydrogen, still contains CO at a fairly high concentration. Thus the development of a technology that will transform this CO into CO₂, which is harmless to platinum electrode catalysts, and reduce the CO concentration in the fuel has become essential.

[0008]

As a means to reduce the CO concentration in the fuel gas (hydrogen-containing gas such as a refined gas) to solve the problem described above, the application of the shift reaction (aqueous shift reaction) shown below is considered.

[0009]



However, by this reaction alone, the reduction in the CO concentration is limited due to the restriction imposed by chemical equilibrium. In general, it is difficult to bring down the CO concentration below 1%.

[0010]

As a means to reduce the CO concentration, introduction of oxygen or air into the refined gas and the use of a CO-selective oxidizing catalyst that oxidizes CO to CO₂ are considered.

[0011]

For CO oxidizing catalysts, Pt/alumina, Pt/silica, Pt/carbon, and Pd/alumina have been known. The temperature at which these catalysts oxidize CO selectively is low (below 100°C). For oxidation processing of gases containing a large quantity of water (such as a refined gas), it is desirable to maintain the reaction temperature above 100°C for reasons such as preventing water aggregation. Furthermore, the CO oxidation reaction is an exothermic process and it is difficult to maintain the temperature of the catalytic layer below 100°C.

[0012]

At temperatures over 100°C, the CO-selectivity of conventional catalysts is reduced: it becomes impossible to reduce the CO concentration in the refined gas to 10 ppm [or somewhat higher] to advance the hydrogen oxidation reaction.

[0013]

In Patent Publication No. 9-30802, a Pt-Ru/Al₂O₃ catalyst is proposed as one that selectively augments the oxidation reaction with CO and offers a very high reaction efficacy.

[0014]

Pt and Ru on the carrier of this catalyst exert their characteristics as metals: on Pt, a reverse shift reaction (shown below) occurs and CO that is generated forms CH₄ through a methanation reaction on Ru. As a result, the CO concentration is reduced.

[0015]

Reverse shift reaction: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$

Methanation reaction: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$

[0016]

[Problem to be solved by the present invention]

To carry out the procedure described above in a satisfactory manner, temperatures over 160°C or preferably over 200°C, are required. In this temperature range, the oxidation of hydrogen occurs rapidly over Pt that has been methanated by hydrogen. Thus together with the methanation reaction over Ru, extensive consumption of hydrogen results in a relative increase in CO concentration. As the fuel for a fuel cell, this procedure is considered inappropriate.

[0017]

The operating temperature for low-temperature-operating fuel cells (especially solid high polymer electrolyte-type fuel cells) is below 100°C. To raise it above 200°C for the suitable fuel gas described above, a very large condenser unit is required for efficient heat recovery, which would present a problem in an automobile, which requires compact devices.

[0018]

[Purpose of the Present Invention]

The present invention was designed to circumvent the problem associated with conventional products. It purports to offer a CO-selective oxidizing catalyst in hydrogen gas, which can selectively oxidize CO at a relatively high temperature (over 100°C). Here the aggregation of _____

water contained in the gas—which is composed mainly of hydrogen but also includes CO and water—is prevented so that the CO concentration of the hydrogen gas may be sufficiently reduced, and a method to manufacture such catalysts.

[0019]

The present invention also purports to offer a method to remove the CO contained in hydrogen gas by using a CO-selective oxidizing catalyst in the hydrogen gas. This method offers hydrogen gas for fuel cells in which the CO concentration has been sufficiently reduced; and such hydrogen gas can be used as fuel for hydrogen-oxygen-type fuel cells, especially low temperature-operating fuel cells (e.g., macromolecular electrolyte-type fuel cells). By adopting

this method, CO poisoning of the fuel electrodes of a generator may be prevented; the life of the cell may be prolonged; and its output stability may be improved.

[0020]

[Method to solve the above-stated problem]

The CO-selective oxidizing catalyst contained in hydrogen gas is, as stated in Claim 1, characteristically composed of a complex oxide of a base metal containing a platinum group metal and a rare earth metal and is dispersed through activated alumina over the surface of a composite ceramic carrier.

[0021]

In applying the CO-selective oxidizing catalysts contained in hydrogen gas of the present invention, as stated in Claim 2, the platinum group metals are palladium and ruthenium.

[0022]

In applying the CO-selective oxidizing catalysts contained in hydrogen gas of the present invention, as stated in Claim 3, the palladium is in the form of palladium chloride, palladium nitrate, or dinitrodiamine palladium; and the ruthenium is either ruthenium chloride or ruthenium nitrate.

[0023]

In applying the CO-selective oxidizing catalysts contained in hydrogen gas of the present invention, as stated in Claim 4, the base metal is copper. In applying the CO-selective oxidizing catalysts contained in hydrogen gas of the present invention, as in Claim 5, the rare earth metals are/is cerium and/or neodymium.

[0024]

In applying the CO-selective oxidizing catalyst contained in hydrogen gas of the present invention, as stated in Claim 6, the cerium and/or neodymium in the complex oxide are/is in the form of cerium oxide and/or neodymium oxide; and the maximum X-ray peak of other metal oxides to that of cerium oxide and/or neodymium oxide is less than 0.01.

[0025]

The method to manufacture the CO-selective oxidizing catalyst contained in hydrogen gas of the present invention is defined as follows: as defined by Claim 7, in manufacturing the CO-selective oxidizing catalyst contained in hydrogen gas that is defined by any one of Claims 1 through 6, the complex oxide of a base metal containing a platinum group metal and rare earth metal is one that is produced through monoxo carbonate, which is generated from a hydrothermal reaction of a carbonate.

[0026]

For the application of the method of manufacturing the CO-selective oxidizing catalyst contained in hydrogen gas of the present invention, as indicated in Item 8, the platinum group metal salt, copper salt, and rare earth metal salt are processed through a hydrothermal reaction by using heated vapor to form coprecipitates, then sintered in air to obtain a complex oxide of a base metal containing a platinum group metal and a rare earth metal, which are kneaded with activated alumina to form a slurry, applied to a composite ceramic carrier, and sintered in an oxidized gas atmosphere at 350 ~ 500°C.

[0027]

For the method to remove CO from the hydrogen gas of the present invention, as defined by Claim 9, a gas mixture in which oxygen is mixed with a gas containing hydrogen, the major component, and CO, is brought into contact with the CO-selective oxidizing catalyst that is defined by any one of Claims 1 through 6 for selective oxidation of CO and conversion of the said CO into CO₂ so that CO may be removed from the aforementioned gas that had contained hydrogen (as its major component) and CO.

[0028]

For the method to remove CO contained in the hydrogen gas of the present invention, as defined by Claim 10, the CO-selective oxidizing reaction is allowed to take place in a temperature range of 100 ~ 200°C.

[0029]

[Actions of the present invention]

The CO-selective oxidizing catalyst contained in the hydrogen gas of the present invention is prepared as follows: a complex oxide of a base metal containing a platinum group metal and rare earth metal and activated alumina that effectively disperses the said complex oxide are applied to the surface of a composite ceramic carrier; then carrier thus coated is sintered.

[0030]

The complex oxide of the base metal containing a platinum group metal and rare earth metal used here may be defined as follows: the platinum group metals may be palladium and ruthenium; the base metal may be copper; and the rare earth metal may be cerium and/or neodymium. It may be a spinel-type complex oxide expressed by the following formula:
 $Ce_xCu_y(PM)O_z$ or $Nd_xCu_y(PM)O_z$ (where PM : Pd + Ru)

[0031]

The complex oxide defined above may be prepared as follows: nitrates and/or chlorides of the aforementioned metals are mixed at a specified stoichiometric ratio. This mixture is added to an

ammonium hydrogen carbonate solution to form a carbonate, then monooxy carbonate through a hydrothermal reaction in heated vapor. The product is then sintered in air.

[0032]

The activated alumina that is used as a mixture with this complex oxide may be γ -alumina that is produced by sintering a boehmite alumina hydrate at a temperature such as 750°C while being exposed to an air current. It is desirable that its specific surface area be greater than 100 m²/g when determined by the BET method.

[0033]

Next, a method to manufacture a CO-specific oxidizing catalyst in hydrogen gas of the present invention is described.

[0034]

For the CO-selective oxidizing catalysts in the hydrogen gas of the present invention, the platinum group metals may be palladium and ruthenium; the base metal is copper; and the rare earth metals are cerium and/or neodymium. In this case, the platinum group metals—palladium that is selected among palladium chloride, palladium nitrate, or dinitrodiamine palladium; and the ruthenium is either ruthenium chloride or ruthenium nitrate—are mixed with copper nitrate and cerium nitrate and/or neodymium nitrate in distilled water.

[0035]

First, ammonium hydrogen carbonate is dispersed in distilled water in an autoclave and the aforementioned mixture is added while being stirred. When the entire mixture has been added, water vapor (at a temperature of 120°C for example) is added to the autoclave, which is hermetically sealed.

[0036]

When the internal pressure of the autoclave reaches 1.1 kg/cm² for example, the addition of water vapor is adjusted so the reaction will continue for about 3 hours.

[0037]

After completion of the reaction, the product is filtered, washed, dried, and sintered in air at 300°C (for example) for 2 hours to obtain a complex oxide of base metals containing platinum group metals and a rare earth metal.

[0038]

Next, the complex oxide of base metals containing platinum group metals and a rare earth metal is kneaded with activated alumina and nitrate-type alumina sol. The resultant slurry is applied to a composite ceramic carrier, which is sintered in a combustion gas atmosphere of 400°C (for example) to obtain the CO-selective oxidizing catalyst of the present invention.

[0039]

Next the actions in the present invention are explained.

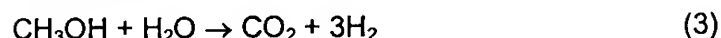
[0040]

A liquid fuel that is composed of water and a refined material that is an alcohol such as methanol is gasified in a carburetor. The product is brought into contact with the refined catalyst; and a hydrogen-rich refined gas is obtained through the vapor-refined reaction shown below.

[0041]



As a whole:



In these reactions, that of formula (1) is endothermic and it is necessary to raise the reaction temperature to improve the conversion rate of methanol. The reaction of formula (2) is exothermic. Because the reaction does not proceed at a high temperature, a large quantity of non-reacting CO remains.

[0042]

If the gas is supplied to a fuel cell as it is, the catalyst (such as platinum) that is used as an electrode is poisoned and the generating potential is reduced. Therefore it is necessary to remove CO contained in the refined gas through oxidation by using a selective oxidizing catalyst until the CO content is reduced to a level of several ppm (for example).

[0043]

By converting the CO into CO₂ through a modifying process by a shift catalyst that performs a shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) as needed, the refined gas reduces the CO concentration to 1,000 [or several thousand] ppm (for example); then it is introduced to the selective oxidizing catalyst layer.

[0044]

The optimum CO-selective oxidizing catalyst used here is defined: in the complex oxide of cerium and/or neodymium, palladium and/or ruthenium are highly effectively dispersed; and due to the high O₂-storage capacity that is associated with rare earth oxides such as cerium and neodymium, palladium and ruthenium can avoid reduction to a metal state even in a hydrogen-rich fuel gas, thus maintaining an oxide state.

[0045]

Thus by merely supplying the amount of air that approximates the theoretically necessary amount of oxygen for an oxidation reaction of CO, the selective oxidation reaction can proceed adequately to accommodate the changes in the CO concentration.

[0046]

CO is oxidized through covalent bonding on oxides such as palladium, ruthenium, and copper, while hydrogen is ionically coordinated on the surface of the metal particles and reacts with oxygen. Thus the hydrogen oxidation reaction is not likely to occur on the aforementioned catalyst, which maintains itself in an oxide state.

[0047]

Even when CO-oxidation, an exothermic reaction, raises the temperature of the catalytic layer over 100°C, CO selectivity is not reduced. Because hydrogen is not likely to be coordinated on the catalytic metal, a reverse shift reaction will not take place.

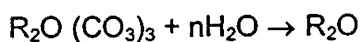
[0048]

Therefore the change in the catalytic layer does not shift the CO concentration in the fuel gas; and due to the exothermic effect of the composite ceramic carrier, the exit temperature of the catalytic layer generally approximates the entry temperature. Thus there is an added advantage of supplying a fuel gas directly to the fuel cell.

[0049]

Through the hydrothermic reaction by using heated water vapor, part of the carbonate radicals ($-\text{CO}_3$) of the cerium and neodymium carbonates is hydrolyzed, generating monoxycarbonates as shown below. These carbonates form hydrates composed of fine crystalline structures.

[0050]



Although in a hydrated state, its structure already has covalently bonded oxygen atoms. Thus an oxide is generated at a low temperature and it is possible for the product to have a large specific surface area.

[0051]

The copper, palladium, and ruthenium that co-exist in the catalyst are also dispersed in the fine crystals of cerium and neodymium. Because the ratio of the maximum X-ray peak of other metal oxides to those of cerium and neodymium oxides is set below 0.01, the catalyst is unaffected by the direct reducing effect of hydrogen, can maintain a highly dispersed state as an oxide for a long time, retains CO-selectivity, and continues to act as a CO-selective oxidative catalyst.

[0052]

[Effects of the present invention]

For the CO-selective oxidative catalyst in the hydrogen gas of this invention, as stated in Claim 1, a complex oxide of base metals that include platinum group metals and rare earth metals are dispersed over the surface of a composite ceramic carrier via activated alumina. Even though in a fuel gas designed for a hydrogen-rich fuel cell, for example, a complex oxide containing platinum group metals is not reduced to a metal state but is constantly maintained in an oxide state. Thus if an amount of air close to the theoretical volume of oxygen that is necessary for the oxidation reaction of CO is supplied, selective oxidation of CO can be conducted adequately in response to changes in the CO concentration. The catalyst is equipped with an outstanding effect to yield hydrogen gas in which the CO concentration is sufficiently reduced. For example, a fuel cell for a vehicular system, which uses hydrogen-rich gas that is obtained by refining methanol, can be produced on a commercial basis. The product will have a notable effect by permitting the use of an alternative fuel and contributing further to the prevention of environmental pollution.

[0053]

As stated in Claim 2, the platinum group metals are palladium and ruthenium. Thus the catalyst has an outstanding effect by improving its catalytic function as a selective oxidizing catalyst for CO in a hydrogen gas.

[0054]

As stated in Claim 3, the palladium is in the form of palladium chloride, palladium nitrate, or dinitrodiamine palladium; and ruthenium is in the form of ruthenium chloride or ruthenium nitrate. Thus it is unlikely that the palladium and ruthenium are reduced to metal states. Instead, the oxide forms can be maintained for an extended period and the catalyst is equipped with an outstanding effect of retaining a steady CO-selective oxidizing activity.

[0055]

As stated in Claim 4, the base metal is copper. Thus the platinum group metals (such as palladium and ruthenium) can be highly effectively dispersed in the complex oxide of rare earth metals (such as cerium and neodymium) and copper. The platinum group metals resist reduction to a metal state. The design has an outstanding effect in minimizing temporal deterioration of the CO-selective oxidative catalyst.

[0056]

As stated in Claim 5, the rare earth metals are cerium and/or neodymium. Because of the high O₂ storage capacity of these rare earth metals (e.g., cerium and neodymium), the platinum group

metals are not reduced to a metal state even in a hydrogen-rich fuel gas, thus offering outstanding effects, such as constantly maintaining an oxide state and enabling CO-selective oxidizing reactions in response to changes in the CO concentration.

[0057]

Furthermore, as stated in Claim 6, cerium and/or neodymium in the complex oxide are in the form of cerium oxide and neodymium oxide. Because the ratio of the maximum X-ray peak of other metal oxides to those of cerium oxide and/or neodymium oxide is below 0.01, the latter are not likely to be reduced directly by hydrogen. Thus the invention offers a marked advantage in maintaining a highly dispersed state as an oxide for a prolonged period, minimizing temporal changes in the selective oxidation reaction, and rendering the complex oxide superior in structural stability.

[0058]

According to the method of manufacturing the CO-selective oxidizing catalyst in the hydrogen gas of the present invention, as described in Claim 7, the complex oxide of a base metal containing platinum group metals and rare earth metal is produced, in the process of preparing the CO-selective oxide catalyst in the hydrogen gas as described in any one of Claims 1 through 6, through monooxy carbonate that is formed in a hydrothermal reaction of the carbonate. Due to the hydrothermal reaction using heated water vapor, part of the carbonate radical ($-\text{CO}_3$) of cerium and neodymium carbonates is hydrolyzed, generating monooxy carbonate and constituting a hydrate state. They can form rare earth complex oxides having a delicate crystalline structure. For example, Pd and Ru are taken up into fine crystals such as Cu-Ce and Cu-Nd; and the O_2 storage capacity of Ce and Nd maintains the stable state for PdO and RuO. Thus the catalyst is equipped with a superior effect in suppressing the methanation or reverse shift reaction, which would otherwise occur on the metals, even at temperatures above 100°C.

[0059]

As stated by Claim 8, platinum group metal salts, copper salt, and rare earth metals are allowed to form coprecipitates through a hydrothermic reaction using heated water vapor; then they are sintered in air to form a complex oxide of base metals containing platinum group metals and rare earth metals. This complex oxide is kneaded with activated alumina to form a slurry. This is applied to a composite ceramic carrier, which is sintered at 350 ~ 500°C in an atmosphere of oxidizing gas. In this manner, heat generated through the oxidation reaction can be efficiently released through the composite ceramic carrier. The method allows the manufacture of a CO-selective oxidizing catalyst, in which the complex oxide of base metals containing platinum

group elements and rare earth metals is effectively dispersed through activated alumina, and which is superior in catalytic functions, with minimal temporal deterioration in these functions.

[0060]

According to the method to remove CO from the hydrogen gas of the present invention, as described by Claim 9, a gas mixture in which oxygen is mixed with a gas containing hydrogen (the major component) and CO is brought into contact with the CO-selective oxidizing catalyst defined by one of Claims 1 through 6 for selective oxidization of CO and converting CO into CO₂ so that CO is removed from the gas containing hydrogen (the major component) and CO. By supplying air in an amount approximating the theoretical quantity of oxygen that is necessary for the oxidation of CO, the CO-selective oxidation reaction is allowed to take place, corresponding to the changes in the CO concentration. Thus the method is associated with an outstanding effect in obtaining a hydrogen gas in which the CO concentration is sufficiently reduced.

[0061]

As described in Claim 10, the CO-selective oxidation reaction is allowed to take place in a temperature range of 100 ~ 200°C. Thus the method is associated with an outstanding effect in preventing the aggregation of water that is in the gas containing CO and water; and in reducing sufficiently the CO concentration of the hydrogen gas by selective oxidation of CO.

[0062]

[Examples]

Examples of application of the present invention, together with comparative examples, are presented below.

[0063]

(Example 1) In an autoclave of 1,000 ml capacity, 158 g of ammonium hydrogen carbonate and 200 ml of distilled water were placed. While stirring, a solution prepared by 1.0 g of palladium chloride (PdCl₂·2H₂O), 1.65 g of ruthenium chloride (RuCl₄·5H₂O), 38.03 g of copper nitrate [Cu(NO₃)₂·3H₂O], and 275.8 g of cerium nitrate [Ce(NO₃)₃·6H₂O] were dissolved in 200 ml of distilled water. The solution was gradually added. When all of the solution had been added, the autoclave was sealed; and while stirring, water vapor at a temperature of about 120°C and vapor pressure of 2 kgf/cm² was injected under pressure. When the internal pressure of the autoclave reached 1.1 kgf/cm², the supply of water vapor was temporarily suspended.

[0064]

While the volume of the water vapor was adjusted to maintain the internal autoclave pressure of 1.1 kgf/cm² (maximum, 1.2 kgf/cm²), stirring was continued for 3 hours to complete the hydrothermic reaction.

[0065]

After 3 hours, the supply of water vapor was completely arrested. The autoclave valve was gradually released and the apparatus was cooled to room temperature while the contents were being stirred. After cooling, the hydrate, in a slurry form when the reaction had been completed, was removed from the autoclave, subjected to a suction filtration process, and the resultant precipitates recovered. Next, the precipitates thus recovered were washed in distilled water and dried in an oven at 100°C for 12 hours.

[0066]

Next, the dried powder was sintered at 300°C for 2 hours while being exposed to an air current to obtain cerium-type complex oxide powder of platinum group metals. The weight of this complex oxide powder was identical to the theoretical quantity (123 g). The specific surface area was 120 m²/g according to the BET method.

[0067]

Into a magnetic ball mill put the total amount of this cerium-type complex oxide powder containing platinum group metals, 100 g of γ -alumina powder (Condia Company, SBa-200, Germany; specific surface area, 180 m²/g), and 200 g of boehmite nitrate sol (a sol prepared by adding 10 weight % of nitric acid to 10 weight % suspension of boehmite alumina) and a slurry obtained by mixing and pulverizing this mixture was applied several times to a composite ceramic carrier (volume, 0.5 L; cell count, 400).

[0068]

The carrier was dried at 130°C for one hour and sintered at 400°C for 2 hours in a combustion gas atmosphere containing a sufficient quantity of oxygen to obtain catalyst A of example 1.

[0069]

The amount of the alumina-containing oxide of the catalyst that had been prepared and applied to the carrier was set at 100 g/piece. As shown in Table 1, in catalyst A, all (Pd, 0.20 g; Ru, 0.20 g; Cu, 4.2 g; and Ce, 37.1 g) were borne on the carrier in the form of oxides.

[0070]

(Example 2)

Except for the use of 2.0 g of palladium chloride, 3.3 g of ruthenium chloride, 38.03 g of copper nitrate, and 272.7 g of cerium nitrate, the procedure of Example 1 was repeated to obtain cerium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder obtained here was 123 g, which was identical to the corresponding theoretical value.

[0071]

Using this complex oxide powder, catalyst B was obtained through a procedure identical to that given in Example 1. As shown in Table 1, all (Pd, 0.416 g; Ru, 0.416 g; Cu, 4.2 g; and Ce, 36.7 g) were borne by the carrier in the form of oxides.

[0072]

(Example 3)

Except for the use of 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 19.0 g of copper nitrate, and 291.35 g of cerium nitrate, the procedure followed in Example 1 was repeated to produce a cerium-type complex oxide containing platinum group metals. The weight of the complex oxide powder thus produced was 122.9 g, which was identical to the corresponding theoretical quantity.

[0073]

By using this complex oxide powder, catalyst C was produced in the manner described in Example 1. As shown in Table 1, in catalyst C, Pd (0.20 g), Ru (0.20 g), Cu (2.08 g), and Ce (39.2 g) were all borne on the carrier in the form of oxides.

[0074]

(Example 4)

Except for the use of 2.0 g of palladium chloride, 3.3 g of ruthenium chloride, 19.0 g of copper nitrate, and 288.3 g of cerium nitrate, the procedure of Example 1 was employed to obtain a cerium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder thus produced was 122.9 g, which was identical to the corresponding theoretical value.

[0075]

By using this complex oxide powder, catalyst D was produced in the manner described in Example 1. As shown in Table 1, in catalyst D, Pd (0.416 g), Ru (0.416 g), Cu (2.08 g), and Ce (38.8 g) were all borne on the carrier in the form of oxides.

[0076]

(Example 5)

Except for the use of 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 38.03 g of copper nitrate, and 270.4 g of neodymium nitrate [$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], the procedure of Example 1 was employed to obtain a neodymium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder thus produced was 117.5 g, which was identical to the corresponding theoretical value.

[0077]

By using this complex oxide powder, catalyst E was produced in the manner described in Example 1. As shown in Table 1, in catalyst E, Pd (0.21 g), Ru (0.21 g), Cu (4.28 g), and Nd (38.0 g) were all borne on the carrier in the form of oxides.

[0078]

(Example 6)

Except for the use of 2.0 g of palladium chloride, 3.3 g of ruthenium chloride, 38.03 g of copper nitrate, and 267.4 g of neodymium nitrate, the procedure followed in Example 1 was employed to obtain a neodymium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder thus produced was 117.6 g, which was identical to the corresponding theoretical value.

[0079]

By using this complex oxide powder, catalyst F was produced in the manner described in Example 1. As shown in Table 1, in catalyst F, Pd (0.425 g), Ru (0.425 g), Cu (4.27 g), and Nd (37.5 g) were all borne on the carrier in the form of oxides.

[0080]

(Example 7)

Except for the use of 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 19.0 g of copper nitrate, and 285.8 g of neodymium nitrate, the procedure of Example 1 was employed to obtain neodymium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder thus produced was 117.2 g, which was identical to the corresponding theoretical value.

[0081]

By using this complex oxide powder, catalyst G was produced in the manner described in Example 1. As shown in Table 1, in catalyst G, Pd (0.21 g), Ru (0.21 g), Cu (2.14 g), and Nd (40.2 g) were all borne on the carrier in the form of oxides.

[0082]

(Example 8)

Except for the use of 2.0 g of palladium chloride, 3.3 g of ruthenium chloride, 19.0 g of copper nitrate, and 282.7 g of neodymium nitrate, the procedure of Example 1 was employed to obtain a neodymium-type complex oxide powder containing platinum group metals. The weight of the complex oxide powder thus produced was 117.2 g, which was identical to the corresponding theoretical value.

[0083]

By using this complex oxide powder, catalyst H was produced in the manner described in Example 1. As shown in Table 1, in catalyst H, Pd (0.426 g), Ru (0.426 g), Cu (2.14 g), and Nd (39.7 g) were all borne on the carrier in the form of oxides.

[0084]

(Comparative Example 1)

Into a 1,000 ml-capacity glass beaker, 158 g of ammonium hydrogen carbonate was placed, together with 200 ml of distilled water. While stirring, a solution, which was prepared by dissolving 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 38.03 g of copper sulfate, and 275.8 g of cerium nitrate in 200 ml of distilled water, was slowly added; and when all of the solution had been added, stirring of the mixture was continued at room temperature for 3 hours, after which slurry-like precipitates were removed from the beaker and subjected to suction-filtration to recover the precipitates.

[0085]

Next, the precipitates that had been recovered were washed in distilled water and dried in an oven at 100°C for 12 hours.

[0086]

Next, the dry powder was sintered at 300°C while being exposed to an air current. A platinum group metal containing cerium-type oxide powder was obtained. The oxide powder thus obtained weighed 123 g, which coincided with the corresponding theoretical volume. According to the BET method, its specific surface area was 85 m²/g.

[0087]

Using this oxide powder and according to the method of Example 1, catalyst I was obtained. In Catalyst I, as shown in Table 1, Pd (0.20 g), Ru (0.20 g), Cu (4.20 g), and Ce (37.1 g) were borne on the carrier, generally in the form of an oxide.

[0088]

(Comparative Example 2)

Except for the use of 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 38.03 g of copper nitrate, and 270.4 g of neodymium nitrate, the procedure given in Comparative Example 1 was repeated to obtain a platinum group metal-containing neodymium-type oxide powder. The oxide powder thus prepared weighed 117.5 g, which coincided with the corresponding theoretical value.

[0089]

Using this oxide powder, catalyst J was prepared as in Example 1. In this catalyst J, Pd (0.21 g), Ru (0.21 g), Cu (4.28 g), and Nd (38.0 g) were borne on the carrier, generally in the form of oxide (Table 1).

[0090]

(Example 9)

Except for the use of 1.0 g of palladium chloride, 1.65 g of ruthenium chloride, 57.0 g of copper nitrate, and 260.4 g of cerium nitrate, the procedure of Example 1 was repeated to obtain a platinum group metal-containing cerium-type complex oxide powder. The complex oxide powder thus prepared weighed 123.2 g, which coincided with the corresponding theoretical value.

[0091]

Using this complex oxide powder, catalyst K was prepared as in Example 1. In this catalyst K, Pd (0.208 g), Ru (0.208 g), Cu (6.25 g), and Ce (35.5 g) were borne on the carrier all in oxide form.

[0092]

[Table 1]

Classification	Manufacturing method	Code for catalyst	Metal components of catalysts (g/catalyst)				
			Ce	Nd	Cu	Pd	Ru
Example 1	Carbon hydrothermal method	A	37.1	-	4.2	0.20	0.20
Example 2	Carbon hydrothermal method	B	36.7	-	4.2	0.416	0.416
Example 3	Carbon hydrothermal method	C	39.2	-	2.08	0.20	0.20
Example 4	Carbon hydrothermal method	D	38.8	-	2.08	0.416	0.416
Example 5	Carbon hydrothermal method	E	-	38.0	4.28	0.21	0.21
Example 6	Carbon hydrothermal method	F	-	37.5	4.27	0.425	0.425
Example 7	Carbon hydrothermal method	G	-	40.2	2.14	0.21	0.21
Example 8	Carbon hydrothermal method	H	-	39.7	2.14	0.426	0.426
Comparative Example 1	Carbonate method	I	37.1	-	4.20	0.20	0.20
Comparative Example 2	Carbonate method	J	-	38.0	4.28	0.21	0.21
Example 9	Carbon hydrothermal method	K	35.5	-	6.25	0.208	0.208

[0093]

(Test example)

For catalysts A through J obtained from Examples 1 through 8 and Comparative Examples 1 and 2, the desired structural stability of the complex oxides were evaluated based on the temporal changes in the CO-selective oxidation reaction and the quantity of CH₄ formed under the conditions shown below.

[0094]

[Table 2]

Conditions for evaluation	
Parameters	Contents
Gas composition	CO : 1% O ₂ : 2% CO ₂ : 25% Water : 0.7% N ₂ : 7.5% H ₂ : the remainder
Temperature	100°C at the gas intake
Gas space velocity (SV)	10,000 Hr ⁻¹
Timing for CO and CH ₄ concentration determination at the catalyst exit	5, 10, 20, 30, 40, 50, and 60 minutes after
Analytical device	Automobile exhaust gas analytical device (CO and HC analyzer)

[0095]

The results are shown in Figure 1.

[0096]

As shown in Figure 1, catalysts I and J, which were obtained from Comparative Examples 1 and 2, were associated with fairly large temporal changes in the CO-selective oxidative reactions and the amounts of CH₄ generated. Catalysts A through H obtained from Examples 1 through 9 of this invention are associated with little temporal change in the CO-selective oxidative reaction or the amount of CH₄ generated. It was recognized that the structure of these complex oxides is highly satisfactory.

[0097]

The X-ray diffraction peaks of catalyst A (Example 1) and catalyst K (example 9) are shown in Figures 2 and 3, respectively. Sequential changes in CO-selective oxidation reactions and CH₄ generation of catalysts A and K are shown in Figure 4.

[0098]

As shown in Figure 4, sequential changes in the CO-selective oxidation reaction and in the amount of CH₄ generated by catalyst K are not quite as comparable to those of catalysts I and J of the aforementioned Comparative Examples 1 and 2 but do increase somewhat. It was noted from the X-ray diffraction peaks of catalysts A and K (shown in Figures 2 and 3), that it is desirable that the ratio of the maximum X-ray peak of other metal oxides (CuO here) to that of cerium oxide (or neodymium oxide) be less than 0.01.

[Brief Explanation of Drawings]

[Figure 1]

A graph shows the temporal changes in CO-selective oxidative reactions and the amount of CH₄ generated when catalysts A through H of Examples 1 through 8 of the present invention and catalysts I and J obtained from Comparative Examples 1 and 2 were used.

[Figure 2]

A graph showing the X-ray diffraction peaks of catalyst A obtained from Example 1 of the Present Invention.

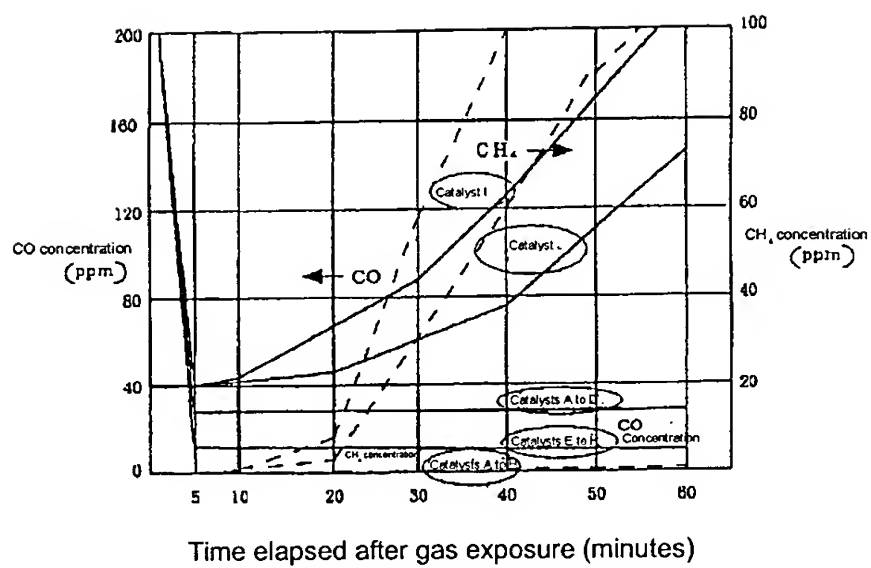
[Figure 3]

A graph showing the X-ray diffraction peak of catalyst K obtained from Example 9 of the present invention.

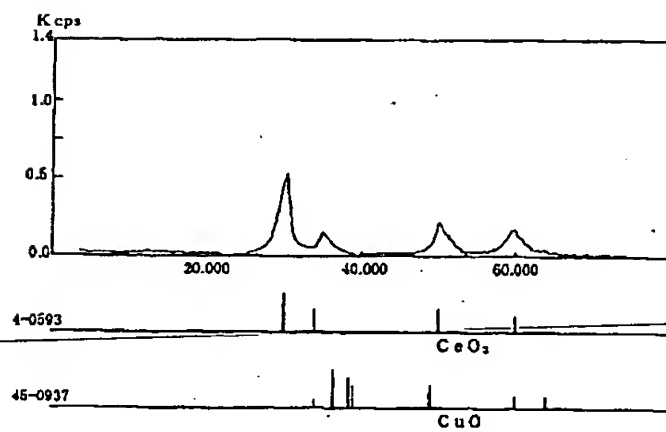
[Figure 4]

A graph displaying sequential changes of the CO-selective oxidation reaction and the amount of CH₄ generated when catalysts A and K obtained from Examples 1 and 9 of the present invention were examined.

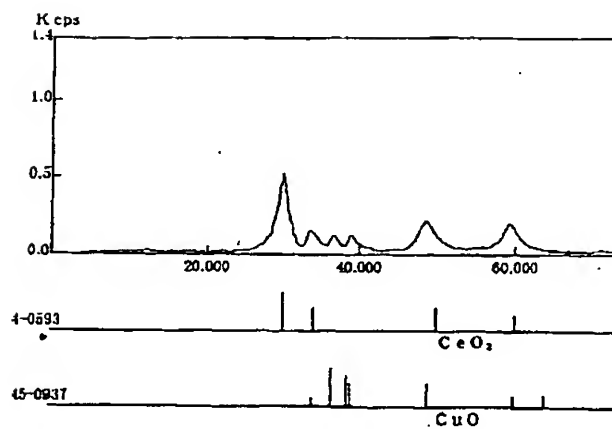
[Figure 1]



[Figure 2]



[Figure 3]



[Figure 4]

